



Degradation of phenolic aqueous solutions by high frequency sono-Fenton systems (US-Fe₂O₃/SBA-15-H₂O₂)

D.H. Bremner^a, R. Molina^{b,*}, F. Martínez^b, J.A. Melero^b, Y. Segura^b

^a School of Contemporary Sciences, University of Abertay Dundee, Dundee DD1 1HG, Scotland, United Kingdom

^b Department of Chemical and Environmental Technology, School of Experimental Sciences and Technology, Rey Juan Carlos University, 28933 Móstoles, Madrid, Spain

ARTICLE INFO

Article history:

Received 29 January 2009

Received in revised form 17 March 2009

Accepted 21 March 2009

Available online 31 March 2009

Keywords:

Ultrasound

Sono-Fenton

Phenol

SBA-15

ABSTRACT

The aim of this work is to establish the influence of different ultrasonic frequencies ranging from 20 to 1142 kHz on the efficiency of the US/Fe₂O₃/SBA-15/H₂O₂ (sono-Fenton) system. The frequency of 584 kHz has been established as the optimum ultrasonic irradiation for the degradation of aqueous phenol solutions by the sono-Fenton system and the effect of different variables, such as hydrogen peroxide concentration or catalyst loadings in the reaction was studied by factorial design of experiments. Catalyst loadings of 0.6 g/L and hydrogen peroxide concentration, close to the stoichiometric amount, show high organic mineralization, accompanied by excellent catalyst stability in a wide range of concentrations of aqueous phenol solutions (0.625–10 mM). Additionally, the catalyst can be easily recovered by filtration for reuse in subsequent reactions without appreciable loss of activity. The coupling of US (584 kHz)/Fe-SBA-15/H₂O₂ at room temperature is revealed as a promising technique for wastewater treatment. Additionally, a new sono-Fenton variant, the so-called latent remediation has also been studied, using ultrasonic irradiation only as pretreatment for 15 min in an attempt at reducing the cost of the degradation process. It has been observed that latent remediation provides TOC degradation of around 21% after 15 min sonication followed by 6 h silent reaction while the typical sono-Fenton reaction affords 29% TOC reduction after 6 h sonication.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Over the last few years, great attention has been paid to the use of ultrasound as one of many potential wastewater treatment technologies [1,2]. Acoustic cavitation takes place due to the propagation of ultrasonic waves through liquids at frequencies ranging from 15 kHz to a few MHz. The collapse of the cavitation bubbles generated by ultrasound irradiation leads to formation of hotspots with extremely high local conditions of temperature and pressure, which allow the formation of reactive radicals, such as H[•], HO[•], O₂^{•-}, as well as the homolytic splitting of polluted compounds. In the range of frequencies mentioned above, 20 kHz ultrasound has been the most widely studied in wastewater treatments but the main drawback of ultrasound alone as a wastewater treatment is the low degradation and mineralization rates of organic compounds, especially in the case of phenol and substituted phenols [3]. Several authors have reported different ways for the intensification of the cavitation phenomena in order to increase the decomposition efficiency and to reduce the time required for removing the pollutants. Thus, in the case of degradation controlled by free

radicals in the liquid phase, the use of different oxidants, such as ozone or hydrogen peroxide, enhance the hydroxyl radical generation, with a subsequent increase in the degradation rates [4,5]. Additionally, the activity of the combined ultrasound/H₂O₂ system can be improved by using catalysts which promote the conversion of hydrogen peroxide into hydroxyl radicals. Particularly, the presence of iron and an ultrasound/H₂O₂ system combine acoustic cavitation with Fenton-like reactions increasing hydroxyl radical generation in a so-called sono-Fenton oxidation system. In this way, promising results have been reported in the literature for the use of homogeneous and heterogeneous sono-Fenton systems in the mineralization of 3-chlorophenol [6], MTBE [7], *p*-chlorobenzoic acid [8] and 2,4-dinitrophenol [9], 4-chlorophenol [10] and phenol [11]. Particularly, studies have been focused on the combination of heterogeneous Fenton-like catalysts with ultrasound in order to overcome the low degradation rate of ultrasound alone without any of problems of homogeneous catalysts in which final precipitation treatments are necessary for the removal of soluble iron ions, with the consequent increase in operation costs. Our research groups have recently described a novel composite Fe-containing SBA-15 mesostructured material (Fe₂O₃/SBA-15) which exhibits high activity and stability in the oxidation of phenolic aqueous solutions by coupling of 20 kHz ultrasound irradiation with heterogeneous Fenton-like oxidation [12,13].

* Corresponding author. Tel.: +34 91 488 80 95; fax: +34 91 488 70 68.
E-mail address: raul.molina@urjc.es (R. Molina).

An additional way to increase the efficiency of acoustic cavitation is to use high frequencies instead low frequencies (between 20 and 100 kHz). It is well recognized that cavitation is less violent at higher frequencies reducing its mechanical effects (hydraulic shear forces and jet streams) that enhance mass transfer, dispersion and disaggregation of catalyst particles. However, it is also known that more cavitation events occur at higher frequencies, providing more opportunities for the free radicals to be produced [14]. Therefore, high frequency would be preferable in ultrasonic oxidation systems involving free radicals, such as hydroxyl radicals, as oxidizing agents. In this way, Berlan et al. [15] reported the benefits of 541 kHz irradiation as compared to 20 kHz in the catalytic decomposition of phenol and Petrier and Francony [16] established that between 20 and 500 kHz, 200 kHz was the most effective frequency for destroying phenol in aqueous solution. The benefits of high frequency for the degradation of other phenolic compounds, such as *p*-cresol, *p*-nitrophenol or *p*-chlorophenol, have also been described [17–19].

The current work is focused on the study of the benefits of combining high frequencies with Fe₂O₃/SBA-15 in a Fenton-like system (sono-Fenton at high frequency) on the oxidation of aqueous phenol solutions, as compared to the sono-Fenton at 20 kHz. Different values of frequencies ranging between 300 and 1150 kHz, have been studied in order to determine the optimum ultrasonic irradiation to maximize efficiency of degradation. Additionally, multivariate analysis has been used to assess the conditions (oxidant and catalyst concentrations) that yield the best results in terms of organic degradation and catalyst stability. The possibility of recovering and reusing the heterogeneous catalyst in subsequent reactions has been also studied. Finally, due to high operation cost of ultrasonic reactors, a new variant of latent remediation has been investigated wherein the sonication time has been kept to a minimum to reduce the overall operational costs of the oxidation treatment.

2. Experimental

2.1. Fenton-like catalyst preparation and characterization

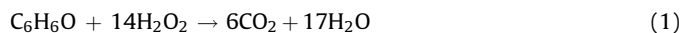
The material employed as heterogeneous catalyst (Fe₂O₃/SBA-15) can be described as a composite that contains mainly crystalline hematite embedded into a mesostructured SBA-15 silica support. The properties of the matrix are characteristic of a hexagonally mesostructured SBA-15 material, with a BET area around 470 m²/g and a narrow pore diameter distribution centred at 7 nm, with iron oxide particles having a wide size distribution (30–300 nm) and well dispersed ionic iron species within the siliceous framework. This material was prepared by co-condensation of iron (FeCl₃·6H₂O; Aldrich) and silica (tetraethoxysilicate, TEOS; Aldrich) under acidic conditions and templated with Pluronic 123 and has a total iron content of about 16 wt.% [20].

2.2. Sono-Fenton set-up

Sono-Fenton reactions were carried out in a glass reactor surrounded by a cooling jacket to control temperature inside the reactor. Ultrasonic irradiation was provided by a transducer system (Meinhardt Ultraschalltechnik) coupled with an HM 8030-6 ultrasonic amplifier, capable of outputting frequencies between 382 and 1.4 MHz. Ultrasonic irradiation is produced from a transducer sited at the bottom of the glass reactor which allows a more regular distribution of energy into the reactor, as compared with a probe system [21]. In this work, the ultrasonic generator was operated in a pulse mode (4 s on and 2 s off) using three different frequencies (382, 584 and 1142 kHz). High frequency sonication does not produce appreciable mechanical or mixing effects and consequently a mechanical stirrer was introduced in

order to assure the homogeneity and the good dispersion of the catalyst in the reaction medium (Fig. 1).

The actual sonication time was 4 h although the real time was 6 h due to operation in the pulsed mode. In a typical experiment, the cylindrical glass reactor was filled with 200 mL of aqueous phenol solution (2.5 mM equivalent to [TOC]₀ = 179.0 ppm) and appropriate amounts of hydrogen peroxide, ranging between 0.58 and 4.76 g L⁻¹. These hydrogen peroxide concentrations are equivalent to 0.5 and 4 times the stoichiometric amount for the complete mineralization of phenol to CO₂ and H₂O according to reaction (1).



An appropriate loading of catalyst (0.2–1.0 g L⁻¹) was suspended in the resultant aqueous solution, the temperature was set at 25 ± 2 °C and the pH was adjusted to ca. 3 with H₂SO₄ (0.1 M). Aliquots were withdrawn throughout the reaction time and filtered through 0.22 μm nylon membranes before analysis. The total organic carbon (TOC) content of the samples was determined using a combustion/non dispersive infrared gas analyzer (1020A; O-I Analytical). Phenol and aromatic degradation products obtained from the partial oxidation of phenol were determined by use of a GC–MS chromatograph (QP2010S from Shimadzu) and hydrogen peroxide concentration was measured by iodometric titration. Iron content in the filtered solution after reaction was measured by a colorimetric process (DR/2400 Spectrophotometer, Hach Company). The iron dissolved in the medium was transformed into soluble ferrous iron by digestion with FerroVer Iron reagent (Hach Company) and then reacted with the 1,10-phenanthroline reagent to form a red-orange colour and the absorbance was measured at 510 nm.

3. Results and discussion

3.1. Preliminary experiments

The efficiency of the sono-Fenton process, based on the combination of 20 kHz ultrasonic irradiation with Fe₂O₃/SBA-15

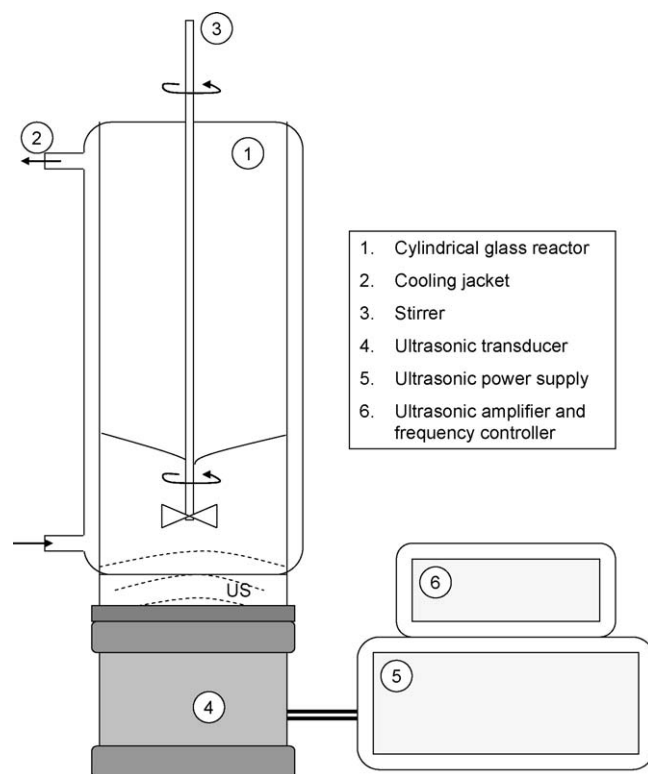


Fig. 1. Schematic representation of the sono-Fenton set-up.

heterogeneous catalyst and hydrogen peroxide has been widely studied by our research group [12,13]. However, the influence and possible benefits of the combination of other ultrasonic frequencies and sonication systems with the heterogeneous Fenton system has not yet been established. In order to determine the influence of the ultrasonic frequency in the sono-Fenton process, reactions were performed at 382, 584 and 1142 kHz. The intensity of the irradiation was adjusted to 50% of ultrasonic power amplitude, and inlet ultrasonic power was determined by calorimetric measurements, obtaining values of 0.013, 0.029 and 0.030 W mL⁻¹ for 382, 584 and 1142 kHz, respectively. The reactions were carried out with 0.6 g L⁻¹ of catalyst and a hydrogen peroxide concentration of 1.19 g L⁻¹ (corresponding to the theoretical stoichiometric amount for the complete mineralization of phenol according to reaction (1)). Fig. 2a shows the results of TOC mineralization in the sono-Fenton system at different ultrasonic frequencies, whereas the efficacy of the sonicated systems in the absence of catalyst is depicted in Fig. 2b. The degree of iron leaching from the catalyst after reaction is shown in the boxes of Fig. 2a.

As can be seen from Fig. 2, the highest degradation of the studied frequencies was obtained with 584 kHz. Although the results are not shown in Fig. 2, phenol completely disappears after 30 min when using 584 kHz and typical aromatic by-products of oxidation, such as catechol, hydroquinone or benzoquinones are also not detected after this time. On the other hand, small amounts of phenol, as well as *p*-benzoquinone, are present after 1 h of sonication with 382 or 1142 kHz ultrasound. It is remarkable that the dissipated heat is very similar using 584 and 1142 kHz.

Several literature reports evidence the increase of degradation with ultrasonic frequency [22]. These results can be explained on the basis of the variation in the collapse pressures and temperatures of cavities as the irradiation frequency is increased. The magnitude of the pressure pulse generated when a single cavity implodes increases with the frequency of irradiation. Taking into account that the cavity collapse is adiabatic, increased collapse pressures, naturally promotes an increment of temperature in the cavity that leads to a high number of generated free radicals. This phenomenon can also be related to the increase of dissipated heat for ultrasonic systems with high frequency as can be seen for the cases of 382 and 584 kHz. However, at frequencies higher than 584 kHz, the effects of the cavitation phenomenon seem to be less

efficient as evidenced by the decrease of TOC removal at the highest 1142 kHz frequency. This fact can be explained by considering that the magnitude of the collapse pressures and temperatures in cavitation is related to the number of and size of the generated cavities, which are dependent on the ultrasonic frequency. Thus, in the range of 382–584 kHz, the cavitation seems to be controlled by the increased production of cavitation events, leading to higher collapse pressures and temperatures as can be also deduced from the increased values of dissipated heat. In contrast, the positive effect of frequency by increasing the quantity of cavitation events seem to be offset by the less violent collapse of smaller short half-life cavities, producing a less effective cavitation. This is in agreement with the slight increase of dissipated heat observed with the 1142 kHz frequency in comparison with 584 kHz.

Considering the catalyst stability, it can be seen that the concentration of total iron species after the reaction was below 4.5 mg/L in all cases, being ca. 4.5% of the initial iron content of the catalyst for the particular experiment of 584 kHz irradiation. Interestingly, sonolysis of aqueous phenol solutions at different frequencies in the presence of just hydrogen peroxide (no iron catalyst) does actually result in some mineralization (Fig. 2b) but the values of TOC conversion and oxidation rates are much lower than in the catalytic system.

In order to compare the efficacy of high frequency sono-Fenton systems based on using an external disk transducer with a typical horn probe ultrasonic device of lower frequency, an additional experiment was performed under identical conditions but using a titanium horn probe system immersed in the reaction medium working in a pulse mode (4 s on, and 2 s off) at a fixed frequency of 20 kHz. Results, in terms of TOC conversion and aromatic compound (phenol, catechol, hydroquinone and benzoquinone) degradation are depicted in Fig. 3 and are compared to that obtained at 584 kHz. The results show that over 4 h the 20 kHz system is less effective than sonication at 584 kHz. TOC conversion reaches a value of ca. 20% compared to 30% obtained for the higher frequency system. Additionally, aromatic compounds, mainly catechol, are still detected in the 20 kHz degradation even after 240 min of sonication. The measurement of dissipated heat by the calorimetric technique for the sonication system with the horn probe at 20 kHz was of 0.1 W mL⁻¹, which is ca. three times higher

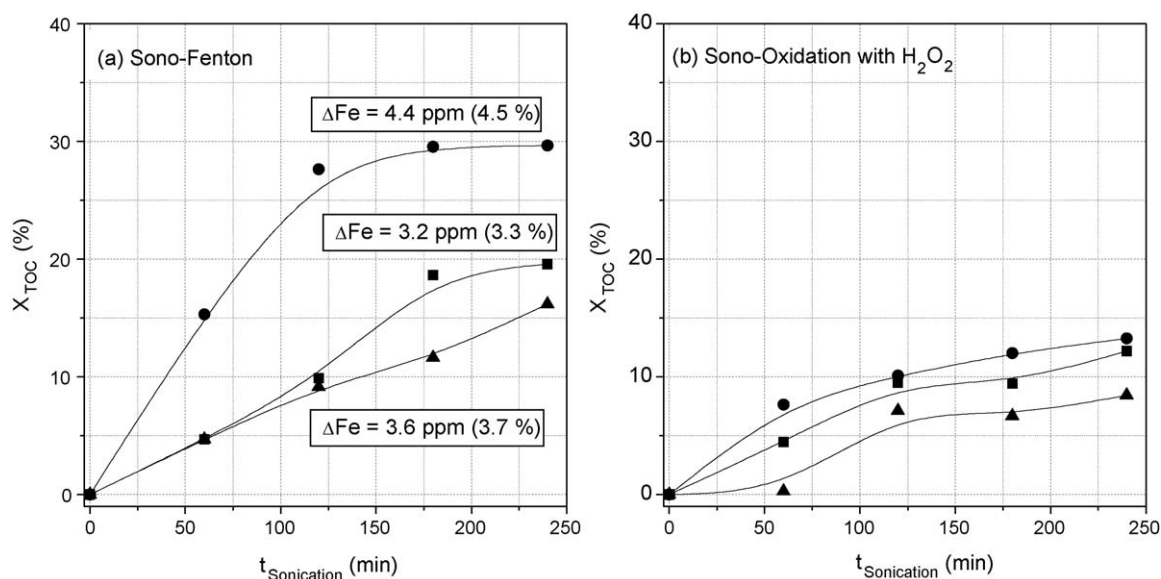


Fig. 2. TOC mineralization of 2.5 mM phenolic aqueous solution at different ultrasonic frequencies ((■) 382 kHz, (●) 584 kHz and (▲) 1142 kHz): (a) Sono-Fenton (iron contents shown in boxes) and (b) Sono-oxidation in absence of the iron catalyst.

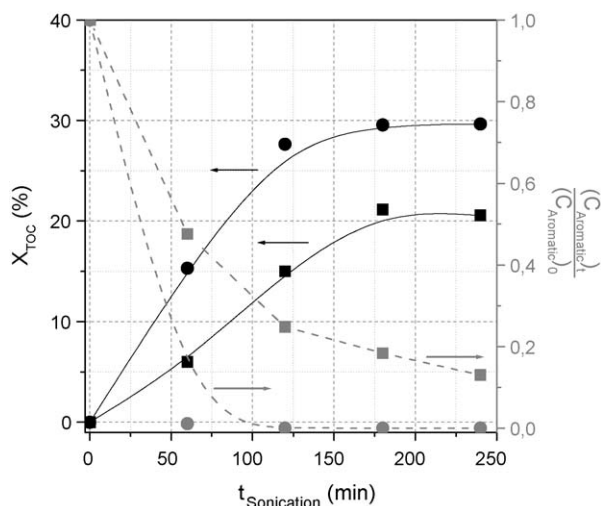


Fig. 3. Comparison of TOC degradation (solid lines) and aromatic compound (phenol, catechol, hydroquinone, benzoquinone) disappearance (dotted lines) at (■) 20 kHz and (●) 584 kHz.

than that obtained for 584 kHz (0.029 W mL^{-1}). This data indicates elevated pressures and temperatures of the cavitation events generated at this low frequency, which does not corroborate the influence of the frequency described previously for sono-Fenton systems with the ultrasonic transducer. This is because the frequency is not the only factor that can produce remarkable variations of the collapse pressure of cavitation events. In fact, it has been already reported that other parameters, such as the acoustic field, the surface area of the sonicator (intensity) and geometry of the reactor can also contribute to the cavitation events and consequently to the overall pollutant degradation [23]. In this sense, the 20 kHz horn probe system is characterized by the formation of axial streams that induce maximum intensities and transfer coefficients on the axis of the ultrasonic beam but which decrease steeply on each side, promoting a better mixing of the reaction medium [24]. Therefore, these particular features of the cavitation field can account for the increase of dissipated heats as compared with the values obtained for the ultrasonic transducer of higher emission surface. However, it must be borne in mind that the high frequency of ultrasonic disk transducer (584 kHz) induces cavitation conditions more effective than the low frequency horn probe (20 kHz) for the production of free radicals that are capable of extending the efficiency of the oxidation reaction, as revealed by the results of TOC conversion for both ultrasonic systems.

3.2. Influence of variables in the sono-Fenton process at 584 kHz

In this research, the influence of two significant variables (catalyst and hydrogen peroxide concentration) on the activity and stability of the sono-Fenton system has been further assessed by means of an experimental design methodology. A complete 3^2 experimental design [25] was performed using catalyst concentrations ranging from 0.2 to 1.0 g L^{-1} , and hydrogen peroxide concentrations from 1.19 to 4.76 g L^{-1} with sonication at 584 kHz as this was seen earlier to be the most effective frequency. The initial pH was adjusted to 3.0 by addition of appropriate amounts of H_2SO_4 solution (0.1 M), the catalyst loadings were selected according to values previously published for the heterogeneous Fenton-like catalyst [26] and hydrogen peroxide concentrations correspond to the stoichiometric and four times the stoichiometric amount respectively. The objective was to minimize the amount of hydrogen peroxide used yet maximize mineralization of phenol to CO_2 and H_2O as measured by TOC conversion during the reaction.

The effect of varying catalyst and hydrogen peroxide concentrations was ascertained by measuring the decrease of TOC at 30, 60, 120, 180 and 240 min. Table 1 shows the codes of the real values for the independent variables studied in the factorial design of experiments.

Factorial design of experiments allows polynomial equations for the prediction of the TOC conversion values in the range of study. Assuming a second order polynomial model and a Levenberg–Marquard algorithm for nonlinear regression, predictive equations for the response variables were produced (Eqs. (2)–(6)). The influence of the independent variables, and their combination, is related to the value and sign of the coefficients of the polynomial expressions.

$$X_{\text{TOC}(30\text{min})} (\%) = 12.0 - 2.0X + 0.5XY - 1.5X^2 - 1.6Y^2 + 5.9XY^2, \\ r^2 = 0.97 \quad (2)$$

$$X_{\text{TOC}(60\text{min})} (\%) = 18.3 - 5.8X + 1.2XY - 3.1X^2 - 2.0Y^2 + 10.6XY^2, \\ r^2 = 0.93 \quad (3)$$

$$X_{\text{TOC}(120\text{min})} (\%) = 23.5 - 5.4Y + 2.1XY - 2.3X^2 - 3.0Y^2 + 4.4YX^2, \\ r^2 = 0.80 \quad (4)$$

$$X_{\text{TOC}(180\text{min})} (\%) = 27.1 + 2.2X - 5.9Y - 2.6X^2 - 5.9Y^2 + 3.9YX^2, \\ r^2 = 0.87 \quad (5)$$

$$X_{\text{TOC}(240\text{min})} (\%) = 26.7 + 1.3X - 6.1Y + 4.2XY - 1.9X^2 - 4.0Y^2 \\ + 4.5XY^2, \quad r^2 = 0.97 \quad (6)$$

Fig. 4 shows the relationship between the experimental data and the predicted values calculated by Eqs. (2)–(6) as they are shown in Table 1. Calculated values are very close to those obtained experimentally, especially at initial (30 and 60 min) and final (240 min) reaction times. The accuracy of the calculated data is in accordance with the correlation factors (r^2) obtained for Eqs. (2)–(6). Additionally, the repeatability of experiments was evaluated on the reaction conditions of the central point (codified as 0, 0 for X and Y variables), estimating a standard deviation of the TOC conversions of ± 2 .

Different effects of the variables can be attested along the reaction time. Thus, the hydrogen peroxide term (Y) does not appear with a negative coefficient until 120 min. This indicates that the increase of only this variable is not beneficial for the maximization of the TOC degradation, in particular, for long

Table 1
Factorial design of experiments.

Experiment	Catalyst (g L^{-1})	Catalyst code (X)	H_2O_2 (g L^{-1})	H_2O_2 code (Y^1)
1	0.2	−1	1.19	−1
2	0.2	−1	2.38	0
3	0.2	−1	4.76	1
4	0.6	0	1.19	−1
5 ^a	0.6	0	2.38	0
6	0.6	0	4.76	1
7	1.0	1	1.19	−1
8	1.0	1	2.38	0
9	1.0	1	4.76	1

^a Central point.

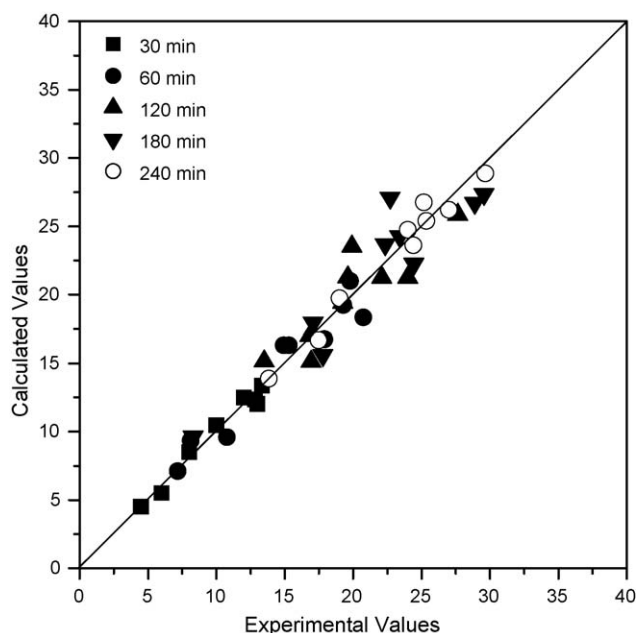


Fig. 4. Accuracy of predicted data from Eqs. (2)–(6) with respect to the experimental TOC conversions.

reaction times. In contrast, for the catalyst term (X), the negative effect exhibited at initial reaction times (30 and 60 min) becomes positive as the reaction proceeds, reinforcing the role of the catalyst in the TOC degradation. Additionally, the terms of the

combined variables (XY , YX^2 and, especially, XY^2) indicate a remarkably positive synergistic effect of both variables with values higher than those observed for the single X and Y terms in most cases. Negative coefficients of quadratic terms for catalyst (X^2) and hydrogen peroxide (Y^2) are characteristic of convex curved surfaces with maximum values of TOC degradation within the range of values studied for each variable. The contribution of each parameter is the result of a complex network of interlinked reactions produced in the combination of ultrasound with Fenton catalytic systems, where hydrogen peroxide can be generated by the presence of the solid catalyst particles under ultrasonic irradiation or decomposed to hydroxyl and hydroperoxyl radicals following the typical chemistry of Fenton reactions. The prevalence of each of the mechanisms in combination with the oxidation reactions of organic compounds control the extent of the TOC degradation in the sono-Fenton process.

In order to clarify the influence of the variables under study, the response curves of TOC conversion arising from Eqs. (2)–(6) are depicted in Fig. 5. As can be seen, the maximum TOC degradation observed for 60 min at the low catalyst loading and intermediate hydrogen peroxide concentration (Fig. 5b) is moved to the range of low/intermediate catalyst and hydrogen peroxide concentrations, corresponding to real values of 0.2 to 0.6 g L⁻¹ and 1.19 to 2.38 g L⁻¹, respectively (Fig. 5c) after 120 min. Similar shapes of the 3D response curves and maximum values of TOC conversion were maintained for 180 and 240 min (Fig. 5d and e).

Finally, it should be pointed out that the sono-Fenton oxidation is a combination of ultrasonic irradiation and a Fenton-like oxidation based on the catalyzed decomposition of H₂O₂ by an iron catalyst to form the highly oxidising hydroxyl radicals. In order to distinguish the benefits of this combined system

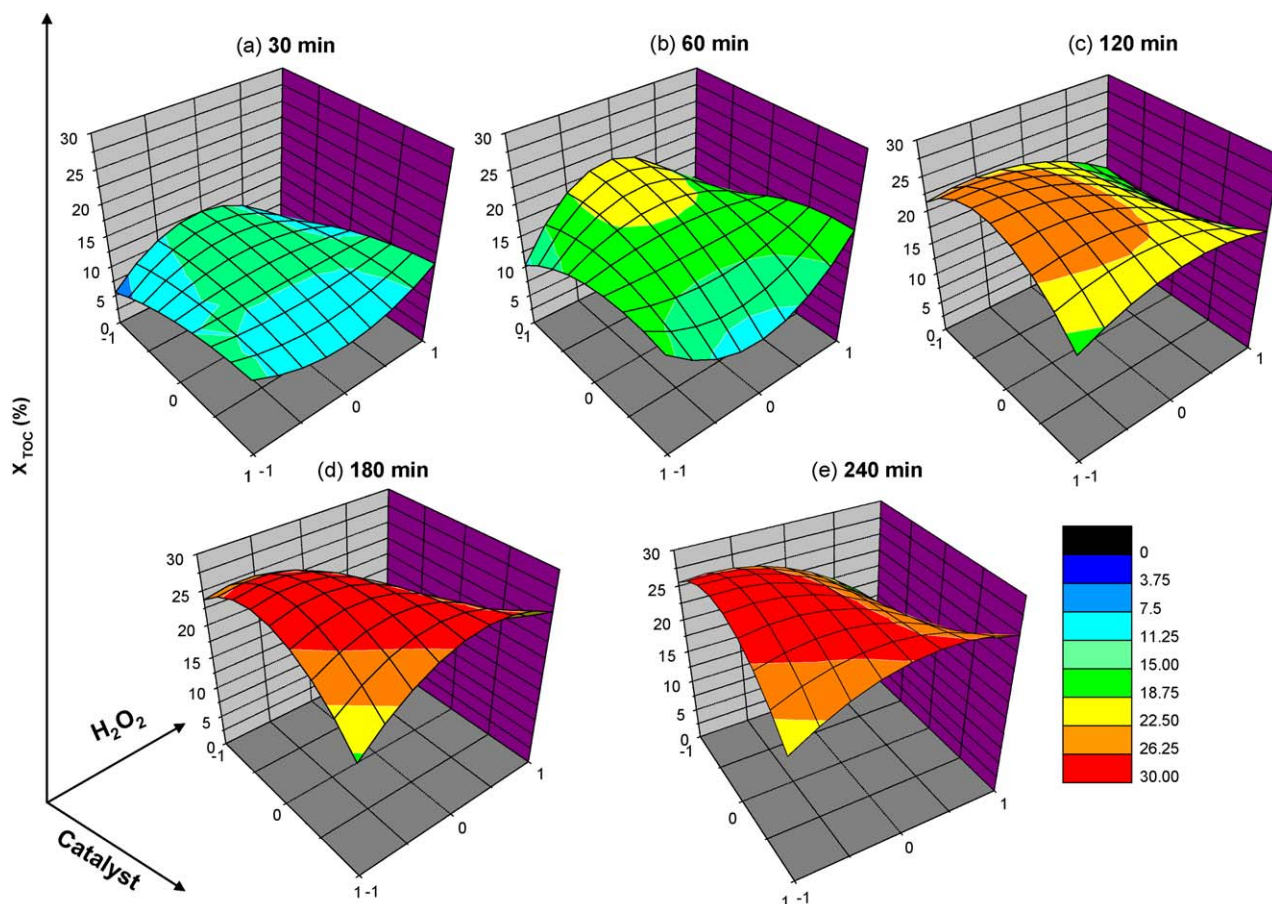
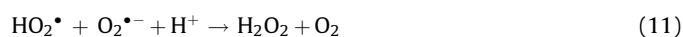


Fig. 5. 3D response surfaces from Eqs. (2)–(6).

compared to a typical Fenton-like oxidation, an additional experiment was carried out under the optimal conditions mentioned previously (0.6 and 1.19 g L⁻¹ of catalyst and hydrogen peroxide, respectively), but in the absence of ultrasound. TOC decrease obtained after this reaction was only ca. 10%, which is significantly lower than the results obtained in the sono-Fenton system.

The oxidant consumption over the reaction time and the iron dissolved in the reaction medium were also studied and are shown in Table 2.

In the case of hydrogen peroxide concentrations of 1.19 and 2.38 g L⁻¹ (codes -1 and 0 in Table 2, respectively) a gradual increase of oxidant use is observed regardless of the catalyst loading as the initial hydrogen peroxide concentration is increased. However, the oxidant conversion for each catalyst loading decreased for the highest amount of hydrogen peroxide (4.76 g L⁻¹, 400% excess of the stoichiometric concentration-code 1). It is remarkable that this decrease of the oxidant consumption coincides with a decrease of TOC degradation and is attributed to the formation of high concentrations of hydroxyl and hydroperoxyl radicals on the catalyst surface in the sono-Fenton process with high excess of the oxidant. According to this hypothesis, the existence of highly concentrated local environments of free radicals on the catalyst surface would make plausible radical recombination to regenerate hydrogen peroxide to the detriment of the oxidation of the organic pollutants (reactions (7)–(11)). Additionally, the competitive reaction of hydroxyl radicals with H₂O₂ to form hydroperoxyl radicals (less oxidative than the hydroxyl radicals) when an excess of the oxidant is used (reaction (12)), must be also taken into account [5].



With respect to stability of the catalyst, a slight decrease in the amount of iron leached was observed as the hydrogen peroxide concentration increased for each catalyst amount. Moreover, the average degree of iron leaching calculated for catalyst loadings of 0.2, 0.6 and 1.0 g L⁻¹ was around 9.0, 3.9 and 4.5%, respectively, indicating a higher stability for intermediate catalyst loadings. Similar trends were also reported for Fe₂O₃/SBA-15 catalyst in the sono-Fenton degradation of phenol aqueous solution with a horn probe working at 20 kHz [12]. Unlike non-ultrasonic Fenton systems, the influence of hydrogen peroxide for a given catalyst

loading is not very significant, producing small variations in iron leaching. In contrast, this difference becomes more important when the catalyst loading is varied at constant hydrogen peroxide concentrations, particularly, for the highest catalyst loading (1 g/L). Nevertheless, it must be pointed out the iron concentrations are very low (3–8 mg/L) in all of the experiments.

Taking into account the above results of the hydrogen peroxide and catalyst concentrations, aqueous solutions with different initial phenol concentrations were also studied in the sono-Fenton process at 584 kHz using 0.6 g L⁻¹ of catalyst loading and a stoichiometric hydrogen peroxide concentration (2.38 g L⁻¹) as optimum values. To the best of our knowledge, studies focused on ultrasonic degradation of organic pollutants, mainly phenolic compounds, relate to aqueous solutions of low concentration such as 2.5 mM (equivalent to 0.235 g L⁻¹ in the case of a phenol solution). Work on higher pollutant concentrations are rare in the literature, although Gogate et al. [22] reported that the degradation of phenol by sonolysis is inversely proportional to the initial concentration in the range 0.1 to 0.5 g L⁻¹. The same behaviour was described by Zhang et al. [27] for the degradation, by ultrasound, of C.I. Acid Orange 7 in the range 0.05–0.25 g L⁻¹ in presence of zero-valent iron. In this study the initial phenol concentration was varied from 0.625 to 10 mM (equivalent to 0.058 and 0.94 g L⁻¹, respectively). Fig. 6 depicts the TOC profiles of the experiments carried out with different initial phenol concentrations and a significant decrease in the TOC degradation when initial concentrations of 7.5 and 10 mM are treated by the sono-Fenton system is observed. For initial concentrations, ranging from 0.625 to 5 mM, the sono-Fenton system exhibited similar degradation results. However, it should be noted that complete phenol removal was obtained in all cases after 30 min of sonication with no other aromatic by-products, such as hydroquinone, catechol or benzoquinone detected, except for 7.5 and 10 mM, where *p*-benzoquinone was still detected at 60 min of sonication. Although solubilised iron was detected in all reactions, this was at levels of 2.8–3.9 mg/L, equivalent to less than 4% of iron species leached out from the catalyst. The decreased catalytic performance of the sono-Fenton system for initial phenol concentrations of 7.5 and 10 mM could be associated with less available active sites as the substrate concentration increases, thus triggering a competitive adsorption onto the catalyst surface [28].

Table 2
Hydrogen peroxide consumption and iron leached out from the catalyst.

Catalyst	H ₂ O ₂	Experimental X _{H₂O₂} (%)				Fe leached out (ppm) after 240 min
		60 min	120 min	180 min	240 min	
-1	-1	6.5	6.5	19.6	23.9	3.6
-1	0	28.5	37.5	55.3	64.2	3.0
-1	1	6.0	29.8	39.0	30.4	3.0
0	-1	12.8	21.3	34.9	42.5	3.9
0	0	36.5	55.7	69.2	61.5	3.1
0	1	4.1	11.8	15.3	18.2	3.0
1	-1	4.2	14.8	17.0	19.1	7.8
1	0	12.2	19.2	22.8	29.8	7.6
1	1	2.9	2.3	8.8	16.5	6.8

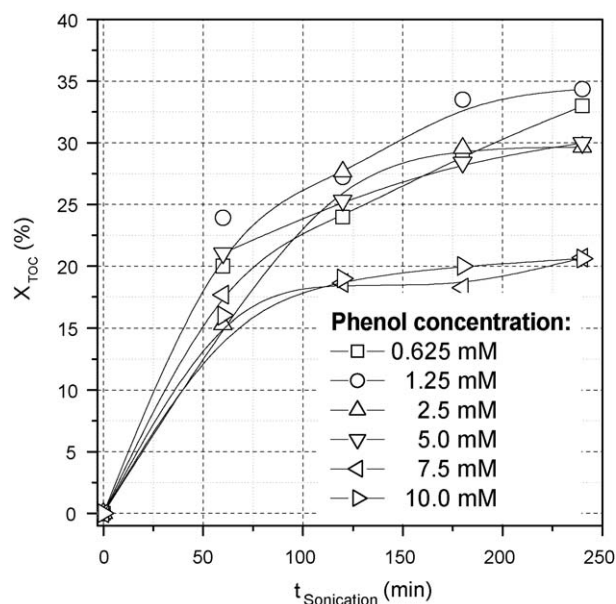


Fig. 6. Influence of the initial phenol solution concentration on the efficiency of the sono-Fenton process.

3.3. Reuse of the $\text{Fe}_2\text{O}_3/\text{SBA-15}$ catalyst at 584 kHz

One of the major advantages of heterogeneous catalysts for environmental application is the possibility of an easy recovery from the reaction medium by physical operations, such as filtration. An additional asset is the possibility of reusing the recovered catalyst with similar successive results of mineralization. Fig. 7 shows the reusability of the $\text{Fe}_2\text{O}_3/\text{SBA-15}$ in the sono-Fenton system. After a reaction carried out at 584 kHz, employing 0.6 and 1.19 g L⁻¹ of catalyst and hydrogen peroxide, respectively (first run is shown Fig. 7), the heterogeneous catalyst was filtered off and dried in an oven at 105 °C. After that, the catalyst was employed in a subsequent reaction under the same conditions as previously used (second run). This process was repeated up to four times and the results, in terms of TOC conversion, are depicted in Fig. 7 with the codes first to fifth run. After using the same catalyst five times, the activity obtained for the system was very similar, and TOC conversion reached values near 30% after 240 min of sonication in all the cases. These results demonstrate the possibility of recovering and reusing the catalyst without appreciable loss of activity in subsequent runs.

Experiments involving recycling of the catalyst in other Fenton-like systems reported in literature show a very different behaviour compared to that obtained in the current sono-Fenton system. In the case of the oxidation of aqueous phenol solutions by thermal Fenton-like oxidation [28], recycled $\text{Fe}_2\text{O}_3/\text{SBA-15}$ exhibits a markedly lower degradation rate as compared with the fresh catalyst. A possible explanation is the deactivating effect of the residual organic compounds adsorbed on the catalyst surface for its reusability in subsequent reactions. In the sono-Fenton system, ultrasonic irradiation induces the formation of liquid jets at the solid surface by the unsymmetrical inrush of the fluid into the collapsing voids [21,29,30] and these jets not only break up the catalyst particles, but also provide surface cleaning, avoiding adsorption of residual organic compounds. In the case of the stability of iron species supported on the SBA-15, a remarkable decrease of the iron leaching was reported in the successive runs for Fenton-like oxidation [28], indicating that the most poorly-bounded iron species (mainly Fe^{3+} ions) were dissolved and lost during the first reaction. In contrast, the concentration of iron leached out from the catalyst in all recycling experiments for the sono-Fenton system studied in this work was ca. 4 mg/L. This

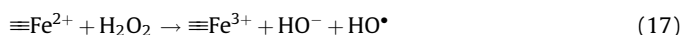
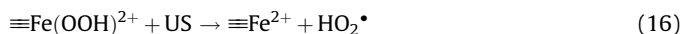
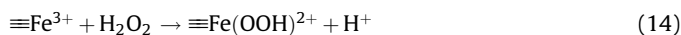
stable and constant iron leaching for the successive reuse of the catalyst confirms the hypothesis suggested earlier, in which the effect of ultrasonic irradiation on the stability of the iron species seems to be more crucial than the oxidizing and acidic conditions that involve the sono-Fenton system.

3.4. Latent remediation

Acoustic cavitation was shown as a promising treatment for the elimination of organic pollutants but the comparatively high cost of treatment has been suggested as a major problem for its application on an industrial scale. For this reason, an emerging alternative to direct sono-Fenton oxidation, the so-called latent remediation, was tested in this work, in order to minimize the operational costs for effective mineralization. In this case, the reaction was carried out under the same conditions as described for the sono-Fenton system, employing 0.6 and 1.19 g L⁻¹ of catalyst and hydrogen peroxide concentrations, respectively. However, ultrasound was applied in a continuous mode (instead pulses of 4 and 2 s) for only 15 min. After this time, part of the reaction medium was filtered to remove the heterogeneous catalyst and both filtered and non-filtered solutions were stored in the dark at room temperature (22 °C) for 6 h. Fig. 8 shows TOC conversions obtained for samples taken after the first 15 min of sono-Fenton conditions and filtered and non-filtered solutions after 6 h of storage are compared to that obtained in the conventional sono-Fenton system (4 h of sonication, equivalent to a total reaction time of 6 h) and silent dark Fenton (6 h with the heterogeneous catalyst at room temperature and absence of any UV-light irradiation).

During the first 15 min of treatment, the extent of TOC diminution was 7% while the remainder occurred in storage (with and without the heterogeneous catalyst still being present in the medium). In the absence of the initial sonication, the TOC reduction hardly reaches 10% after 6 h of reaction. Fig. 8a shows that TOC degradation reaches values of 21 and 12% (in a non-filtered or a filtered case, respectively) after 6 h without any further treatment. The low activity of the filtered case is due to the fact that the only iron present in the aqueous medium is that dissolved during the treatment (less than 3% of total iron contained in the $\text{Fe}_2\text{O}_3/\text{SBA-15}$ material). All the results revealed a significant latent activity of the Fenton-like catalyst under storage conditions that reached approximately the final TOC degradation obtained (29.9%) in a typical sono-Fenton system with ultrasonic irradiation in pulses of 4 s on and 2 s for a total reaction time of 6 h.

Latent remediation can be explained taking into account the effect of the sonication in the reaction medium in the presence of the heterogeneous iron catalyst and hydrogen peroxide. The reaction of ultrasound coupled with the Fenton-like reagent can be described by the following Eqs. (14)–(17) where the symbol \equiv represents iron species bound to the surface of the catalyst.



The use of ultrasound during the first 15 min enhances the transformation of Fe^{3+} to iron Fe^{2+} by reactions (14)–(16) with the production of hydroperoxyl radicals as well as hydroxyl radicals by subsequent typical Fenton reaction of oxidation of Fe^{2+} to Fe^{3+} (reaction (17)). The oxidising species, mainly hydroxyl and hydroperoxyl radicals, so produced then react

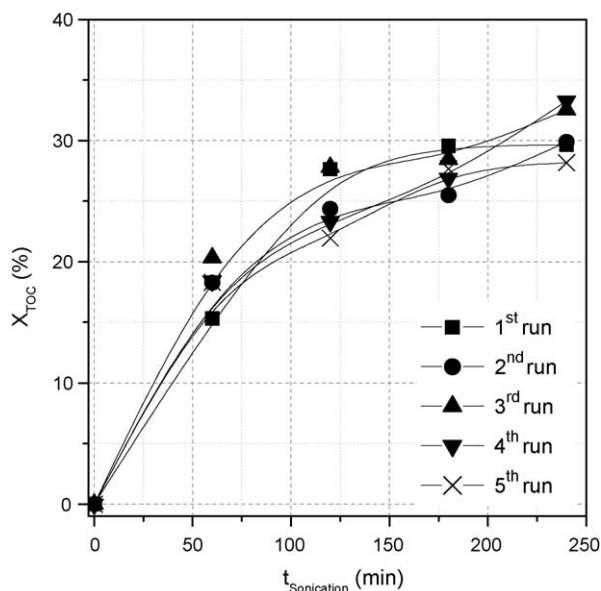


Fig. 7. Reusability of the $\text{Fe}_2\text{O}_3/\text{SBA-15}$ catalyst in the sono-Fenton system.

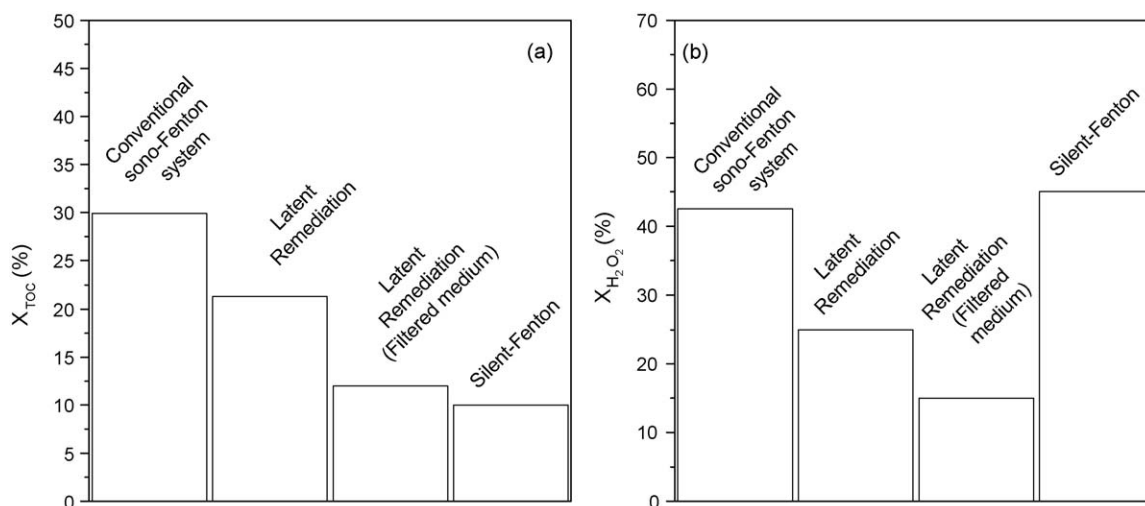


Fig. 8. Comparison of the sono-Fenton system and latent remediation: (a) TOC decrease and (b) hydrogen peroxide consumption after 6 h of total reaction time.

with the organic substrates to give intermediate by-products or complete mineralization.

In the absence of sonication, the reduction of Fe^{3+} to Fe^{2+} (reaction (15)) slows down because reduction of $\equiv Fe(OOH)^{2+}$ by ultrasound doesn't occur (reaction (16)). This is the reason why the activity only reaches values of 10% of TOC degradation after 6 h of reaction in the conditions of silent dark Fenton previously mentioned. The presence of hydrogen peroxide ensures the formation of oxidizing species during the process (reactions (14) and (17)) and it will be consumed in the reaction, as it can be seen in Fig. 8b. A plausible explanation of the increased activity in the latent remediation in presence of the catalyst can be the reduction of the supported-iron catalyst during the 15 min of continuous ultrasonic irradiation leaving part of the iron sites in the reduced form (Fe^{2+}), which would enable an additional production of hydroxyl radicals via the reaction (17). These results of latent remediation based on preliminary US/Fe-SBA-15/ H_2O_2 systems open new possibilities for reducing operational costs of the process and are currently under further investigation.

4. Conclusions

The heterogeneous sono-Fenton system is a promising approach for the treatment of phenol in aqueous solutions. High frequencies, especially 584 kHz, provide a better (X_{TOC}/US_{POWER}) system probably due to promoting the number and distribution of cavitations instead of the formation of microjets and violent local cavitation observed at 20 kHz. The factorial design of experiments carried out at 584 kHz shows that the optimal hydrogen peroxide concentration is the stoichiometric amount in the presence of 0.6 g L^{-1} of $Fe_2O_3/SBA-15$ catalyst and results in values of final TOC degradation of ca. 30%, which represents a low oxidant dosage as compared with similar studies reported in the literature. Additionally, complete destruction of phenol and aromatic by-products can be achieved after 30 min of sonication and a remarkable stability of the Fe-SBA-15 heterogeneous catalyst is also established (less than 4 ppm loss for the best reaction conditions). Furthermore, the possibility of recovering the catalyst by filtration and reusing it up to five times without appreciable loss of activity after drying at 105°C has been demonstrated. The sono-Fenton system can degrade aqueous phenol solutions of concentrations ranging from 0.625 to 5 mM with high efficiency but more concentrated solutions, up to 10 mM, show a decreased reactivity.

Finally, the combination of the sono-Fenton system followed by latent remediation results in ca. 21% TOC degradation after 15 min of sonication followed by 6 h of silent reaction while the typical sono-Fenton system affords 29% TOC reduction after 6 h of sonication. This result opens new possibilities for reducing operational costs of ultrasonic systems.

Acknowledgments

Financial support of Regional Government of Madrid provided through the project "Red Madrileña de Tratamientos Avanzados de Aguas Residuales con Contaminantes no biodegradables" (REMTA-VARES) and the Spanish Government provided through projects CTM2005-01053 and CONSOLIDER INGENIO 2010 program is gratefully acknowledged. R. Molina thanks Ministerio de Ciencia e Innovación for a research fellowship through the José Castillejo Program. Y. Segura is also grateful to the Juan de la Cierva program. The authors also acknowledge support from the EU COST D32 programme.

References

- [1] Y.G. Adewuyi, Environ. Sci. Technol. 39 (2005) 3409–3420.
- [2] P.R. Gogate, Adv. Env. Res. 6 (2002) 335–358.
- [3] R. Kidak, N.H. Ince, Ultrason Sonochem. 13 (2006) 195–199.
- [4] J.G. Lin, C.N. Chang, J.R. Wu, Y.S. Ma, Water Sci. Technol. 34 (1996) 41–48.
- [5] F. Chemat, P.G.M. Teunissen, S. Chemat, P.V. Baartels, Ultrason. Sonochem. 8 (2001) 247–250.
- [6] Y. Nagata, M. Nakagawa, H. Okumo, Y. Mizukoshi, B. Yim, Y. Maeda, Ultrason. Sonochem. 7 (2000) 115–120.
- [7] B. Neppolian, H. Jung, H. Choi, J.H. Lee, J.-W. Kang, Wat. Res. 36 (2002) 4699–4708.
- [8] B. Neppolian, J.-S. Park, H. Choi, Ultrason. Sonochem. 11 (2004) 273–279.
- [9] Z. Guo, Z. Zheng, S. Zheng, W. Hu, R. Feng, Ultrason. Sonochem. 12 (2005) 461–465.
- [10] J. Liang, S. Komarov, N. Hayashi, E. Kasai, Ultrason. Sonochem. 14 (2007) 201–207.
- [11] A.N. Nikolopoulos, O. Igglessi-Markopoulou, N. Papayannakos, Ultrason. Sonochem. 13 (2006) 92–97.
- [12] R. Molina, F. Martínez, J.A. Melero, D.H. Bremner, A.G. Chakinala, Appl. Catal. B: Environ. 66 (2006) 198–207.
- [13] A. Juan, F. Melero, R. Martínez, Molina, J. Adv. Oxid. Technol. 11 (2008) 75–83.
- [14] Y.G. Adewuyi, Ind. Eng. Chem. Res. 40 (2001) 4681–4715.
- [15] J. Berlan, F. Trabelsi, H. Delmas, A.M. Wilhelm, J.F. Pettrigiani, Ultrason. Sonochem. 1994 (1994) 97–102.
- [16] C. Petrier, A. Francony, Ultrason. Sonochem. 4 (1997) 295.
- [17] M. Entezari, C. Petrier, Appl. Catal. B: Environ. 53 (2004) 257.
- [18] C. Petrier, Y. Jiang, M.F. Lamy, Environ. Sci. Technol. 32 (1998) 1316.
- [19] H. Hua, Y. Chen, M. Wu, H. Wang, Y. Yin, Z. Lü, Ultrason. Sonochem. 11 (2004) 43.
- [20] K. Lazar, G. Calleja, J.A. Melero, F. Martínez, R. Molina, Stud. Surf. Sci. Catal. 154 (2004) 805–812.
- [21] T.J. Mason, J.P. Lorimer, Applied Sonochemistry. The Uses of Power Ultrasound in Chemistry and Processing, Wiley-VCH, 2002.

- [22] P.R. Gogate, S. Mujumdar, J. Thampi, A.M. Wilhelm, A.B. Pandit, Sep. Purif. Technol. 34 (2004) 25–34.
- [23] M.H. Entezari, C. Pétrier, P. Devidal, Ultrason. Sonochem. 10 (2003) 103–108.
- [24] F. Faïd, F. Contamine, A.M. Whilhem, H. Delmas, Ultrason. Sonochem. 5 (1998) 119–124.
- [25] G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for Experiments, an Introduction to Design, Data Analysis and Model Building, John Wiley and Sons, New York, 1978.
- [26] F. Martínez, G. Calleja, J.A. Melero, R. Molina, Appl. Catal. B: Environ. 60 (2005) 185–194.
- [27] H. Zhang, L. Duan, Y. Zhang, F. Wu, Dyes Pigments 65 (2005) 39–43.
- [28] J.A. Melero, G. Calleja, F. Martínez, R. Molina, I. Pariente, Chem. Eng. J. 131 (2007) 245–256.
- [29] Y.G. Adewuyi, Environ. Sci. Technol. 39 (2005) 8557–8570.
- [30] P.R. Gogate, Ultrason. Sonochem. 15 (2008) 1–15.